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Hydrogen–Deuterium Randomization in 7-Methyl-4-octanone-7-d_1 at Times of 10^{-11}–10^{-5} Sec Following Field Ionization

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Abstract: Partial hydrogen–deuterium (H–D) randomization occurs prior to the McLafferty rearrangement in 7-methyl-4-octanone-7-d_1 following field ionization (FI) even at times as short as the order of 10^{-11} sec. This behavior contrasts sharply with that of straight-chain ketones in which no H–D randomization occurs prior to the McLafferty rearrangement at times $<7 \times 10^{-10}$ sec. At times of 10^{-11}–10^{-10} sec following FI the rate of the McLafferty rearrangement is an order of magnitude smaller in 7-methyl-4-octanone than in a typical straight-chain ketone 2-octanone, but at $\sim 10^{-6}$ sec the situation is reversed with the rate being an order of magnitude smaller in the straight-chain ketone. The difference in kinetics is consistent with the McLafferty rearrangement at times > a few $\times 10^{-11}$ sec following FI being a stepwise rather than a concerted process. It is proposed that H–D randomization in the 7-methyl-4-octanone-7-d_1 ion involves γ-D transfer to the oxygen forming a tertiary radical, followed by reverse D transfer from the oxygen to the alkyl chain. The reverse transfer is facilitated by the stability of the tertiary radical.

The unimolecular gas-phase reactions induced by electron impact (EI) of aliphatic ketones have been studied intensively.[2] The behavior of aliphatic ketones following field ionization (FI) has also received considerable attention.[3–6] Mass spectra of partially deuterated straight-chain aliphatic ketones produced by EI at ordinary ionizing voltages (70 eV) reveal little hydrogen–deuterium (H–D) randomization,[7] although a degree of randomization is manifested in the metastable region[8] (corresponding to molecular ion lifetimes of 10^{-6} sec). At very low ionizing voltages (10–12 eV) a degree of H–D randomization is also evident in the normal EI mass spectra.[7,8] These observations have been rationalized on the basis that the randomization reactions in straight-chain aliphatic ketones have low

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(2) For a review of the early studies, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 3.

(3) A. J. B. Robertson and B. W. Viney, *Advan. Mass Spectrom.*, 3, 23 (1966).

(4) F. W. Röllgen and H. D. Beckey, *Surface Sci.*, 23, 69 (1971).

(5) E. M. Chait and F. G. Kitson, *Org. Mass Spectrom.*, 3, 533 (1970).

(6) P. J. Derrick, A. M. Falick, S. Lewis, and A. L. Burlingame, *Org. Mass Spectrom.*, 7, 887 (1973).

(7) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, 90, 160 (1968).

(8) (a) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Commun.*, 1269 (1968); (b) A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, 91, 3582 (1969).

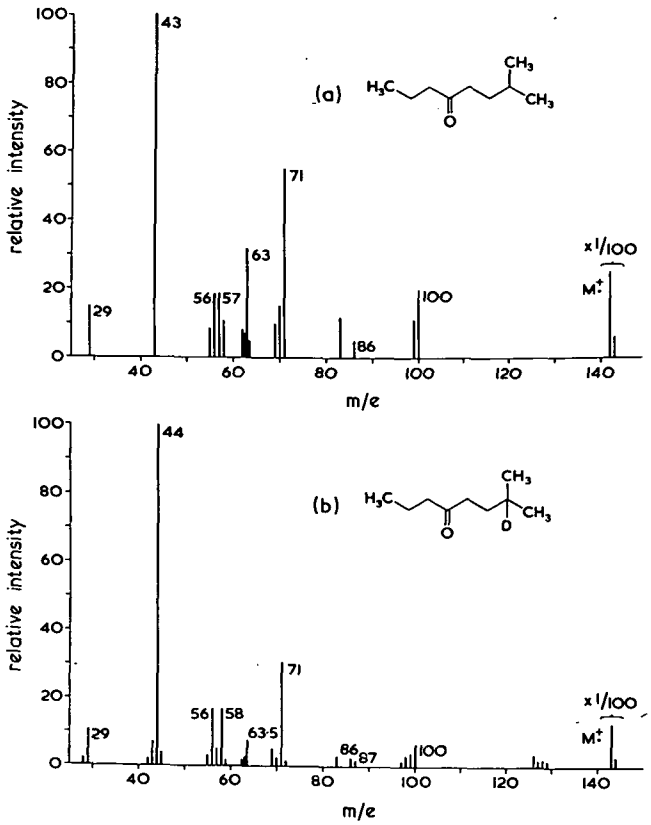


Figure 1. The "normal" FI mass spectrum of (a) 7-methyl-4-octanone; (b) 7-methyl-4-octanone-7-d_1. Source temperature 50°. Uncoated Schick blade emitter.

activation energies and frequency factors[8] (employing the concepts of the simplified quasi-equilibrium theory[9]). A study[6] of H–D randomization in 2-octanone-*1,1,1,3,3-*d_5 following FI supports this view. No H–D randomization occurs prior to the McLafferty rearrangement at times less than 7×10^{-10} sec following FI. Partial H–D randomization is observed at times of 10^{-6}–10^{-5} sec. The EI mass spectra of certain branched aliphatic ketones, however, contain evidence of extensive H–D randomization even at ordinary ionizing voltages.[10] Compounds labeled specifically at the γ position seem to exhibit more randomization prior to the McLafferty rearrangement than compounds labeled elsewhere.[10] Branching at the γ position would seem to be more conducive to randomization prior to the McLafferty rearrangement than branching at the δ position.[10]

We have sought to elucidate this difference in behavior between certain branched and straight-chain ketones as regards H–D randomization by studying the randomization following FI in the γ-branched and γ-d-labeled 7-methyl-4-octanone-7-d_1. FI mass spectrometry permits rates of unimolecular gas-phase reactions to be measured at times as short as 10^{-11} sec (or even 10^{-12} sec) and at longer times.[11–16] We shall refer to

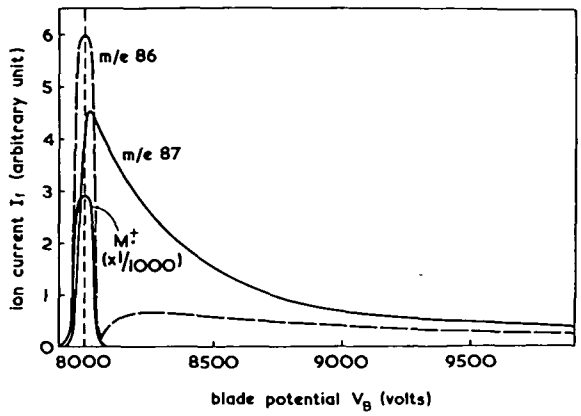


Figure 2. The experimental curves of ion currents I_f against blade potential V_B for the molecular ion and the McLafferty rearrangement products from 7-methyl-4-octanone-7-d_1. Each curve is the average of several runs. Considering, for example, *m/e* 86 between V_B = 8100 V and V_B = 9900 V, fluctuations in any run are of the order of 10% of the signal. Fluctuation is proportionately less for higher ion currents.

such data on rates of reaction from times of 10^{-11} to 10^{-5} sec as "field ionization kinetics (FIK)."[17] The highly resolved (according to time) view of events afforded by FIK can often allow a deeper and more certain understanding of the reactions responsible for H–D randomization than is possible from the integrated view (over some 10^{-6} sec) afforded by EI alone.[17,18]

Results

The "normal" FI mass spectra of 7-methyl-4-octanone and 7-methyl-4-octanone-7-d_1 obtained with a double focusing mass spectrometer are reproduced in Figure 1. EI mass spectra at 70 and 15 eV ionizing energies have been published.[10] "Normal" FI mass spectra, as defined in this paper, are those measured with the potential V_B applied to the blade emitter approximately equal to the accelerating potential (8000 V) necessary for ions to be transmitted through the electric sector analyzer. Thus the "normal" spectra display the ions formed within the very high field in the immediate vicinity of the blade (*i.e.*, at times less than $\sim 10^{-11}$ sec).[16]

Profiles of ion current against blade potential V_B for the molecular ion and the important fragment ions following FI of 7-methyl-4-octanone-7-d_1 are reproduced in Figure 2. The profiles are measured on an XY recorder by focusing the magnetic analyzer on a particular ion and sweeping the blade potential.[16] The theory behind the measurement and interpretation of such profiles has been discussed in detail elsewhere (see, for example, ref 14, 16, and 17). The measured profiles of ion current I_f against blade potential for the fragment ions can be transformed to curves of ion current $I_f(t)$ against molecular ion lifetime[16,19] (Figure 3). The fragments of *m/e* 86 ($C_5H_{10}O$) and *m/e* 87 (C_5H_9DO) are

(9) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U. S.*, 38, 667 (1952).
(10) G. Eadon and C. Djerassi, *J. Amer. Chem. Soc.*, 92, 3084 (1970).
(11) H. D. Beckey, *Z. Naturforsch. A*, 16, 505 (1961).
(12) H. D. Beckey and H. Knöppel, *Z. Naturforsch. A*, 21, 1920 (1966).
(13) H. D. Beckey, H. Hey, K. Levsen, and G. Tenschert, *Int. J. Mass Spectrom. Ion Phys.*, 2, 101 (1969).
(14) P. J. Derrick and A. J. B. Robertson, *Proc. Roy. Soc., Ser. A*, 324, 491 (1971).
(15) K. Levsen and H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, 7, 341 (1971).
(16) A. M. Falick, P. J. Derrick, and A. L. Burlingame, *Int. J. Mass Spectrom. Ion Phys.*, 12, 101 (1973).
(17) P. J. Derrick, A. M. Falick, and A. L. Burlingame, 20th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, 1972, Paper No. H4.
(18) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Amer. Chem. Soc.*, 94, 6794 (1972).
(19) J.-P. Pfeifer, A. M. Falick, and A. L. Burlingame, *Int. J. Mass Spectrom. Ion Phys.*, 11, 345 (1973).

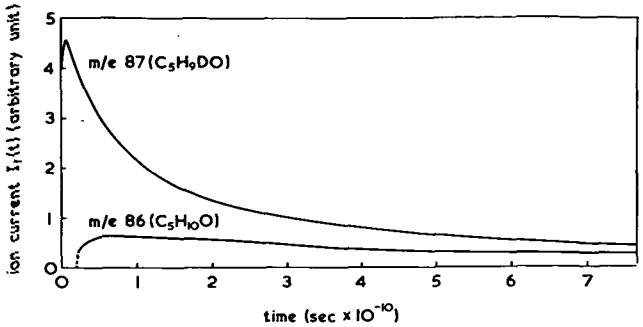


Figure 3. Ion currents $I_f(t)$ of *m/e* 86 ($C_5H_{10}O$) and *m/e* 87 (C_5H_9DO) from 7-methyl-4-octanone-7-d_1 as a function of molecular ion lifetime. The times are derived by mathematical procedure[16] from the blade potentials V_B in Figure 2.

products of the McLafferty rearrangement (see below). The portion of the *m/e* 86 profile at $V_B < 8070$ V in Figure 2 has been disregarded in drawing up Figure 3, since this has probably arisen from a surface process.[20] The ratio of the ion currents $I_f(t)$ for *m/e* 86 and 87 at any particular time is approximately equal to the ratio of their rates of formation at that time.[16,18]

Phenomenological rate constants $\bar{k}(t)$ can be calculated for the formation of a fragment ion from the molecular ion from eq 1 which has been discussed

$$\bar{k}(t) = I_f(t)/I_M\Delta t \qquad (1)$$

fully.[16,18,21] A phenomenological rate constant $\bar{k}(t)$ is an experimental quantity referring to a real situation in which reactant ions exist over a distribution of internal energies. A phenomenological rate constant is distinct from a microscopic rate constant, which is the theoretical quantity referring to the ideal situation in which reactant ions possess some discrete amount of internal energy. Phenomenological rate constants are function of time[16] and are therefore calculated at various reaction times t. $I_f(t)$ is the fragment ion current at any time t and I_M represents the ion current of molecular ion available for reaction at that time. Δt accounts for the fact that fragment ions formed over a small time interval contribute to the measured ion current $I_f(t)$.[16] Phenomenological rate constants for decompositions in the first and second field free region can be estimated by substituting metastable intensities into eq 1 for $I_f(t)$. In Table I the phenomenological rate constants $\bar{k}(t)$ calculated from eq 1 for the formation of *m/e* 86 ($C_5H_{10}O$) from 7-methyl-4-octanone by the McLafferty rearrangement following FI are compared with rate constants calculated in the same way for the McLafferty rearrangement following FI of a typical straight-chain ketone 2-octanone.

The relative intensities of the metastable transitions $143^+ \rightarrow 87^+$ and $143^+ \rightarrow 86^+$ induced by FI of 7-methyl-4-octanone-7-d_1 in the first and second field free regions are shown in Table II. The metastables in the first field free region are measured by defocusing the electric sector analyzer in the normal manner.[22] The figures for the shorter times following FI are taken from Figure 3. Intensities of *m/e* 86 and 87 in the EI mass spectra measured by earlier workers[10] are also shown in Table II.

Table I. Relative Phenomenological Rate Constants $\bar{k}(t)$[a] for the McLafferty Rearrangement Following FI in 7-Methyl-4-octanone[b] and in 2-Octanone[c] (Given Relative to that for the McLafferty Rearrangement in 7-Methyl-4-octanone at 1×10^{-5} sec)

Time, sec	7-Methyl-4-octanone	2-Octanone
7×10^{-11}	1×10^5	8×10^5
7×10^{-10}	8×10^3	6×10^4
2×10^{-6}	8	1.4
1×10^{-5}	1	Undetected

[a] Maximum possible error ±25%. [b] Measurements made at 50°. [c] Measurements made at 25°.

Table II. Relative Intensities of *m/e* 87 (C_5H_9DO) and *m/e* 86 ($C_5H_{10}O$) from 7-Methyl-4-octanone-7-d_1 Following Field Ionization and Following Electron Impact

	m/e 87	*m/e* 86
Theoretical		
Calculated assuming complete H–D randomization (C_1–C_8, and the C-7 methyl)	56	44
Calculated assuming H–D randomization on C_6–C_8 and the C-7 methyl only	11	89
Field ionization		
1×10^{-11} sec	100	0[a]
2×10^{-11} sec	94 ± 1	6 ± 1
1×10^{-10} sec	78 ± 2	22 ± 2
7×10^{-10} sec	67 ± 6	33 ± 6
2×10^{-6} sec (metastables in first field free region)	45 ± 5	55 ± 5
1×10^{-5} sec (metastables in second field free region)	47 ± 10	53 ± 10
Electron impact[10]		
70 eV	65	35
15 eV	61	39

[a] Obtained by extrapolation of the *m/e* 86 curve in Figure 3.

Discussion

The "normal" FI mass spectrum of 7-methyl-4-octanone-7-d_1 (Figure 1b) contains no evidence of H–D randomization.[23] We attribute the *m/e* 86 peak in Figure 1b to a surface process.[20] We conclude that no H–D randomization occurs either within the neutral molecule prior to ionization or within the ionized molecule at times less than $\sim 10^{-11}$ sec following ionization. The fragmentation in the "normal" FI mass spectra of 7-methyl-4-octanone and the deuterated analog conforms to established patterns.[3-6] Fragmentations occurring at times longer than a few $\times 10^{-11}$ sec following FI are gas-phase processes within low external electric fields.[16] Following FI of 7-methyl-4-

(20) The maximum at $V_B = 8000$ V coupled with the symmetrical shape of the profile at $V_B < 8070$ V would indicate this. The evidence to date suggests that *gas-phase* rearrangement is characterized by an ion current–blade potential profile with a maximum at blade potentials higher than that required to produce the "normal" FI mass spectrum. See (a) ref 13; (b) H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, 5, 182 (1970); (c) P. Schulze and W. J. Richter, *ibid.*, 6, 131 (1971); (d) H. D. Beckey, *Z. Naturforsch. A*, 26, 1243 (1971); (e) G. Tenschert and H. D. Beckey, *Int. J. Mass Spectrom. Ion Phys.*, 7, 97 (1971); (f) ref 15; (g) K. Levsen and H. D. Beckey, *ibid.*, 9, 51,63 (1972); (h) ref 16; (i) ref 17; (j) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Amer. Chem. Soc.*, 95, 437 (1973); (k) ref 6.

(21) See H. D. Beckey, "Field Ionization Mass Spectrometry," Pergamon Press, New York, N. Y., 1971, pp 143–180.

(22) For a description, see L. P. Hills and J. H. Futrell, *Org. Mass Spectrom.*, 5, 1019 (1971).

(23) The "normal" FI mass spectra of deuterated hexanals contain no evidence of H–D randomization. See (a) ref 17; (b) P. Brown and C. Fenselau, *Org. Mass Spectrom.*, 7, 305 (1973).

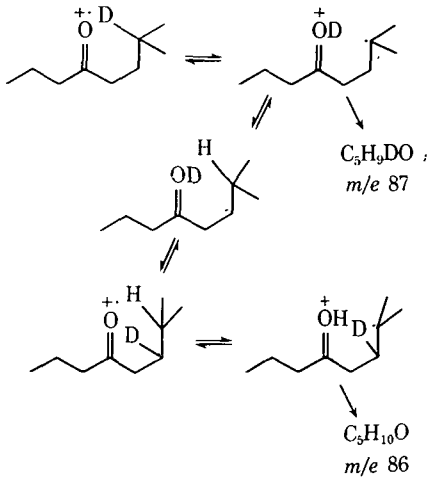
octanone the only significant fragmentation at 10^{-11}–10^{-9} sec is that leading to *m/e* 86 identified as the McLafferty rearrangement. The products of α cleavage, *m/e* 71 and 99, are detected at low intensities. Following FI of 7-methyl-4-octanone-7-d_1 two fragments, *m/e* 87 and 86, are formed at significant intensities at times of 10^{-11}–10^{-9} sec. Both fragments must be attributed to the McLafferty rearrangement. Thus either the McLafferty rearrangement is not specific or partial H–D randomization is occurring prior to fragmentation. The McLafferty rearrangement in ketones following EI is firmly established as being specific to the γ position.[24] There are no grounds for supposing that the McLafferty rearrangement induced by FI differs in this respect.[25] We therefore attribute the *m/e* 86 fragments at times > a few $\times 10^{-11}$ sec following FI of 7-methyl-4-octanone-7-d_1 to partial H–D randomization prior to fragmentation. The *m/e* 86 ($C_5H_{10}O$) ion current (Figure 3) appears to drop sharply to zero at some time of the order of 10^{-11} sec. We interpret this behavior as an indication that there is some lower time limit within which H–D randomization does not occur prior to fragmentation. Since the time resolution of the instrument is finite (about 5×10^{-11} sec for this experiment), the point at which the ion current drops to zero will appear at a somewhat shorter time than its true position. We place the time limit for randomization in the region of 5×10^{-11} sec.

Following FI of 7-methyl-4-octanone-7-d_1 H–D randomization is able to compete successfully with the McLafferty rearrangement even within those ions sufficiently energetic to decompose at times as short as the order of 10^{-11} sec. If the basic tenets of the quasi-equilibrium theory[9] concerning distribution of internal energy within a molecule are valid at such short times for FI and for both high and low energy EI, then the conclusion should also hold for EI. That is to say, following both 70 and 15 eV of 7-methyl-4-octanone-7-d_1 H–D randomization would successfully compete with the McLafferty rearrangement at times of the order of 10^{-11} sec. We suggest that this is the case, and that the unusually high degree of H–D randomization manifest in the normal 70 eV EI mass spectrum can be attributed to this fact. H–D randomization in straight-chain ketones can be seen to compete successfully with fragmentation only at times of the order of 10^{-6} sec following FI.[6]

The relative numbers of *m/e* 87 (C_5H_9DO) and *m/e* 86 ($C_5H_{10}O$) formed by the McLafferty rearrangement within a few $\times 10^{-6}$ sec of FI can be estimated approximately by integrating the rate–time curves (see Experimental Section for details). We find that between 1×10^{-11} and 5×10^{-6} sec following FI the relative proportions of *m/e* 87 (C_5H_9DO) and *m/e* 86 ($C_5H_{10}O$) formed are 60 and 40%, respectively. These figures compare satisfactorily with the relative intensities observed in the EI mass spectra[10] (65 and 35% at 70 eV and 61 and 39% at 15 eV). Relative to the molecular ion intensity I_M, the integrated intensities of *m/e* 87 (C_5H_9DO) and *m/e* 86 ($C_5H_{10}O$) formed between 1×10^{-11} and 5×10^{-6} sec following FI are 0.03 and 0.02, respectively. The degree of fragmentation *via* the McLafferty rearrangement following FI is two orders of magnitude less than that following nominally 15 eV EI.[10] This can be attributed to a smaller amount of excitation energy imparted to the molecules by FI.

That H–D randomization following FI occurs prior to fragmentation at times as short as the order of 10^{-11} sec in 7-methyl-4-octanone-7-d_1 but not in straight-chain ketones can be accounted for on the basis of the mechanism[7] depicted in Scheme I. The mechanism is

Scheme I



proposed for randomization in straight-chain as well as in γ-branched ketones. The McLafferty rearrangement in aliphatic ketones at > a few $\times 10^{-11}$ sec following FI is envisaged as being stepwise[26] (*vide infra*). We suggest that the key to the success of H–D randomization in γ-branched ketones is stability of the tertiary radical a (Scheme I).[10] Consider molecular ions which ultimately decompose *via* the McLafferty rearrangement in times of a few $\times 10^{-11}$ or 10^{-10} sec. These will be ions of relatively high internal energies. We suggest that with a γ-branched ketone the tertiary radical intermediate is sufficiently stable to allow a degree of reverse D transfer from the oxygen to the alkyl chain (Scheme I), whereas with a straight-chain ketone the secondary radical undergoes β cleavage before reverse transfer can occur. With a straight-chain ketone reverse transfer can only compete successfully with β cleavage within lower energy ions decomposing at $\sim 10^{-6}$ sec.[27] Should an H transfer have occurred

(24) (a) S. Meyerson and J. D. McCollum, *Advan. Anal. Chem. Instrum.*, 2, 184 (1963); (b) H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, 22, 1391 (1966).

(25) The evidence[26] to date would suggest that the reactions induced by FI at times $>10^{-11}$ sec are typically the same reactions as are induced by low energy EI (10–12 eV).

(26) The mechanism of the McLafferty rearrangement has been a contentious question. The balance of opinions in recent years would, however, seem to favor stepwise mechanisms. See (a) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Amer. Chem. Soc.*, 90, 7239 (1968); (b) C. Fenselau, J. L. Young, S. Meyerson, W. R. Landris, E. Selke, and L. C. Leitch, *ibid.*, 91, 6847 (1969); (c) J. S. Smith and F. W. McLafferty, *Org. Mass Spectrom.*, 5, 483 (1971). FIK measurements on hexanal suggest that in this molecule the McLafferty rearrangement following FI may be concerted but only at times of a few $\times 10^{-11}$ sec. At longer times the reaction is probably stepwise. See (d) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Amer. Chem. Soc.*, submitted for publication.

(27) The argument here is that low internal energies tend to favor rearrangement over direct bond cleavage. See (a) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Commun.*, 1269 (1968); (b) A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, 91, 3582 (1969). In comparing the γ-branched ketone to the straight-chain ketone, we are employing essentially the same argument. Replacing a secondary radical by a more stable tertiary radical can be regarded as having the same effect as lowering the internal energy. Thus the rearrangement (reverse transfer) is favored over the direct bond cleavage (β cleavage) on introducing branching at the γ position.

within the alkyl chain (or between the alkyl chains) prior to the reverse transfer, a step toward H–D randomization will have been effected.

The hypothesis is corroborated by the FIK data on the McLafferty rearrangements in 7-methyl-4-octanone and straight-chain ketones (Table I). In comparing the two sets of phenomenological rate constants we assume that the internal energy distributions are similar for the two molecules. We consider such an assumption to be reasonable since the two molecules are similar both in their chemical and their physical properties and since all measurements were made with the same emitter at the same field strengths and at similar temperatures. We have made FIK measurements on a large number of straight-chain and branched aliphatic ketones. The kinetics of the McLafferty rearrangement in the γ-branched 7-methyl-4-octanone differ markedly from the kinetics of the rearrangement in straight-chain ketones or branched ketones in which there are secondary hydrogens at the γ position. The phenomenological rate constants for the McLafferty rearrangement in 7-methyl-4-octanone at times of 10^{-11}–10^{-10} sec following FI are approximately an order of magnitude less than the corresponding phenomenological rate constants for 2-octanone. At times of $\sim 10^{-6}$ sec the situation is reversed with the rate constants for 7-methyl-4-octanone being approximately an order of magnitude greater. The total fraction of ions undergoing the McLafferty rearrangement following FI is, however, approximately the same ($\sim 5 \times 10^{-2}$) for both compounds[28] (based on integration of the rate–time curves). The situation can be summarized by saying that although the McLafferty rearrangement is of similar importance in both compounds, it is considerably *slower* in the branched compound.[29] The gross differences between the kinetics of the two McLafferty rearrangements cannot be reasonably explained on the bases of mechanisms representing the reactions as concerted processes. We will thus consider that the reactions occur in a stepwise fashion (at least at times > a few $\times 10^{-11}$ sec). It is unlikely that the differences between kinetics arise in the hydrogen transfers, since it is unreasonable to propose that the transfer of a labile tertiary hydrogen be considerably slower than the transfer of a secondary hydrogen. If the differences between the kinetics do not arise in the hydrogen transfers, they presumably arise in the subsequent β-cleavage steps. The β cleavage in the γ-branched ketone must be slower than that in the straight-chain ketone, which is consistent with the tertiary radical a (Scheme I) being more stable than the corresponding secondary radical in the straight-chain ketone. A slower β cleavage in 7-methyl-4-octanone supports our proposals as to the mechanism of H–D randomization.

Further support for the hypothesis can be marshalled from FIK measurements[30] on 3-methyl-2-heptanone-*1,1,1,3-d*$_4$. It is found that no H–D randomization occurs prior to the McLafferty rearrangement at times less than 1×10^{-9} sec following FI. H–D randomization in this compound following FI bears the same characteristics as that in a straight-chain ketone.[6] This is as would be predicted from the proposed hypothesis, since γ-H transfer in 3-methyl-2-heptanone-*1,1,1,3-d*$_4$ gives rise to a secondary radical.[31] We would point out that the failure of α branching and α labeling to enhance H–D randomization in the same manner as γ branching and γ labeling weighs against mechanisms[8] of the type which involve simultaneous migration of an H and a D effecting a direct exchange.[32]

It remains only to comment on the dependence of the H–D randomization process in 7-methyl-4-octanone upon internal energy *E*. It is clear (Table II) that the degree of H–D randomization prior to the McLafferty rearrangement following FI increases with time. Making the reasonable assumption that reaction time is related in a direct manner to internal energy *E*, it follows that the success of the H–D randomization process in competing with the McLafferty rearrangement increases as internal energy *E* decreases. Following EI the degree of H–D randomization in 7-methyl-4-octanone-*7-d*$_1$ prior to the McLafferty rearrangement does increase to a small extent on lowering the electron energy from 70 to 15 eV (Table II).[33] It is interesting that the intensities of *m/e* 86 ($C_5H_{10}O$) formed in the first and second field-free regions by the McLafferty rearrangement following FI of 7-methyl-4-octanone-*7-d*$_1$ are higher than the calculated intensities for complete H–D randomization (Table II). This probably indicates that complete H–D randomization has not been reached. Partial randomization of just the hydrogens attached to C_6–C_8 and the C-7 methyl, for example, could produce this result. A kinetic isotope effect may also be present, but replacement of γ-H by D does not produce a kinetic isotope effect on the McLafferty rearrangement in aliphatic ketones following 70 eV ionization.[34]

Our discussion has been directly concerned only with reactions induced by FI at times of 10^{-11}–10^{-5} sec. We would suggest, however, that the proposals as to mechanisms of H–D randomization and of the McLafferty rearrangement are equally valid within the same time frame following low energy EI and quite possibly high energy EI.

(28) The degrees of fragmentation *via* the McLafferty rearrangement in the EI mass spectra of 7-methyl-4-octanone and 2-octanone are similar.[7,10]

(29) Some figures based on the aforementioned integration of rate–time curves exemplify this. Only approximately 25% of the total fragmentation of 7-methyl-4-octanone *via* the McLafferty rearrangement following FI occurs in times less than 1×10^{-9} sec, whereas 75% occurs at times longer than 1×10^{-9} sec; the corresponding figures for 2-octanone are 60 and 40%, respectively.

(30) P. J. Derrick, A. M. Falick, and A. L. Burlingame, unpublished data.

(31) δ-Branched and δ-D labeled ketones exhibit enhanced H–D randomization prior to the McLafferty rearrangement but not to the same degree as the γ branched and γ labeled.[10] We would suggest that in this case a process of the type represented in Scheme I is still operative but involving δ transfer *via* a seven-membered cyclic transition state facilitated by the labile D. Hydrogen transfers in carbonyl compounds *via* seven-membered cyclic transition states have been suggested previously. See (a) ref 7; (b) R. J. Liedtke and C. Djerassi, *J. Amer. Chem. Soc.*, **91**, 6814 (1969); (c) M. Kraft and G. Spiteller, *Org. Mass Spectrom.*, **2**, 541 (1969); (d) A. G. Harrison, *ibid.*, **3**, 549 (1970).

(32) FIK and EI measurements on 2-methylpropane suggest that such exchange-type processes do operate with this compound but are favored by high excitation energies (P. J. Derrick, A. M. Falick, and A. L. Burlingame, in preparation for *J. Chem. Soc., Perkin Trans. 2*,) whereas H–D randomization even in γ-branched ketones is favored by low energies.

(33) The extent of H–D randomization prior to α cleavage of 7-methyl-4-octanone-*7-d*$_1$ following EI appears to be independent of electron energy.[10] The reason for this is not obvious from the present experimental data. The effect that varying the electron energy has on the competition between the α cleavages and the McLafferty rearrangement may be relevant to the problem.

(34) J. K. Macleod and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 5812 (1967).

Experimental Section

FIK measurements were made with a modified double focusing Du Pont (CEC) 21-110B mass spectrometer.[16] Uncoated Schick stainless steel razor blades were used as emitters in the standard Du Pont FI/EI ion source. Curves of ion current *vs.* blade potential were measured on an XY recorder. The blade potential was scanned from 8 to 10 kV in steps of 10 V so that the curves are quasi-continuous.

The synthesis of the deuterated compound has been described.[10]

Total fragment ion currents formed between 1×10^{-11} and 5×10^{-6} sec following FI were estimated as follows. The logarithm of the rate constant $\bar{k}(t)$ calculated from eq 1 for the particular reaction of interest was plotted against log t. The resulting graph had a series of points in the range 10^{-11}–10^{-9} sec and two additional points at 1×10^{-5} and 2×10^{-6} sec (from the metastables). A curve was drawn through all these points *interpolating between* 10^{-9} *and* 2×10^{-6} *sec*. With both *m/e* 86 ($C_5H_{10}O$) and *m/e* 87 (C_5H_9DO) from 7-methyl-4-octanone-7-d_1 these curves of log $\bar{k}(t)$ *vs.* log t could be approximated by straight lines. The area under the curves could then be estimated by analytical integration. The area under such a curve represents the total current due to a particular fragment ion (expressed as a fraction of the molecular ion current) formed between the time limits of integration.

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